The University of Chicago

THE PEROXIDE EFFECT UPON THE ADDITION OF HYDROGEN BROMIDE TO UNSATURATED COMPOUNDS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1933

By
ROBERT SAMUEL SHANE

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The author desires to express here his heart-felt gratitude to his father for the opportunity of pursuing the studies presented herein.

The author takes this opportunity to express his appreciation of the invaluable counsel and guidance of Professor M. S. Kharasch of the University of Chicago.

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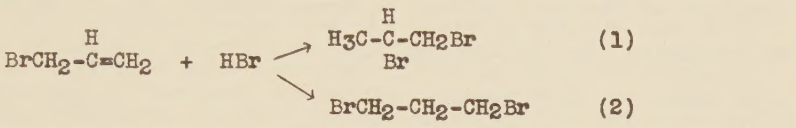
INTRODUCTION

Hydrogen bromide can add to allyl bromide in two ways, i.e., to give either the 1,2 or the 1,3 dibromopropane. It was shown



conclusively by Kharasch and Mayo[1] that the 1,2 dibromopropane is formed to the extent of 90 per cent, if the addition is carried out in the absence of air or oxygen and if allyl bromide free of peroxides is employed. This has been called, therefore, the normal reaction. On the other hand, if the addition is carried out in air, or if the allyl bromide contains some peroxides, or if peroxides are added to the reaction mixture, 1,3 dibromopropane is formed to the extent of 90 per cent. This reaction was termed by the authors the peroxide catalyzed reaction. The authors have shown that the effect of peroxides could be overcome by adding to the reaction mixture small quantities of substances called (for want of better name) anti-oxidants. The net result of the presence of these latter materials was the same as if peroxide-free allyl bromide had been employed and the reaction allowed to proceed in vacuo.[2]

These authors have demonstrated also that temperature, solvents, and light have little or no effect per se on the course of the reaction but merely exaggerate the peroxide effect. In fact, the latter effect is the most important single factor governing directed addition to allyl bromide.

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[1] Mayo, Doctorate dissertation, University of Chicago.
[2] See footnote 8--page 5.

It is quite obvious that in the evolution of any theory of addition of reagents to unsaturated compounds it is of prime importance to be able to differentiate between the normal and the peroxide catalyzed addition. Therefore, a study was undertaken of the addition of hydrogen bromide to allyl chloride and isobutylene. The results were most interesting for it was shown that while the addition of hydrogen bromide to allyl chloride was quite sensitive to peroxides, the mode of addition of hydrogen bromide to isobutylene could not be influenced either by peroxides or anti-oxidants.

PREVIOUS WORK

Table I is a summary of the recorded results of the addition of hydrogen bromide to allyl chloride. The work, while inadequate from many standpoints, points definitely to the fact, which has been stressed in many articles, that the 1,3 chlorobromopropane is the major if not the exclusive product of the addition. We shall show later that the formation of this product is due primarily to the fact that the investigators had failed to carry out the reaction under peroxide-free conditions.

TABLE I

SUMMARY OF PREVIOUS ADDITIONS OF HYDROGEN BROMIDE TO ALLYL CHLORIDE

Light	Temperature	Solvent	Yield	% 1,2	% 1,3	Reference
Not stated	100°	Water	18%	Small	Large	3
Not stated	180°	None	Low	-----	-----	5
Not stated	----	Ether	Poor	Small	Large	4
Not stated	Over warm	Pt black	Poor	Small	Large	4
Sunshine	Room	Moisture	47%	3-4	43	4
Not stated	4°	Water	87.2%	0	87.2	6

[3]Reboul, Ann. chim. phys., (5), 14, 487 (1878).
[4]Bruylants, Rec. trav. chim., 28, 244 (1909).
[5]Lermontoff, see preceding reference.
[6]Putochin, Ber., 55, 2748 (1922).

DISCUSSION OF THE PRESENT WORK

1. Methods of Analysis of the Reaction Mixture

For a quantitative study of the effect of various factors upon the directed addition of hydrogen bromide to allyl chloride it was necessary first to prepare the 1-chloro-2-bromo- and the 1-chloro-3-bromo- propanes in a pure condition. Second, a method of removing allyl chloride from the reaction mixture had to be evolved. Third, a method of analysis of the mixture of the two isomeric substances accurate within three to five per cent had to be perfected. The experimental part contains the details of the three methods. Suffice it to say that fuming (5% SO_3) sulfuric acid was found to be entirely suitable as a selective agent for the removal of allyl chloride from a mixture of the chlorobromopropanes, and that the index of refraction of the mixture was found to be a reliable method for determining the percentages of the two isomeric chlorobromopropanes. Preliminary experiments have demonstrated that the index of refraction is a linear function of the composition. The net error involved in all these methods was five to six per cent, and the results could be readily duplicated providing the factors governing the direction of addition were taken into consideration.

2. Factors Influencing the Addition of Hydrogen Bromide to Allyl Chloride

a. The peroxide effect.- Table II proves quite conclusively that in the presence of air or peroxides hydrogen bromide adds to allyl chloride to give 1,3 chlorobromopropane. As was to be expected, the results in vacuo are slightly irregular, and the irreg-

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[7]Attention is called to the fact that in all these additions liquid hydrogen bromide was added to allyl chloride. This method is much more rapid than the ones employed by previous investigators, namely many saturations at low or ordinary temperatures. For the exact technique see Experimental Part.

TABLE II

STANDARD CONDITIONS*

Run no.	Peroxide** Content	n_D^{20} Crude	n_D^{20} Refined	Yield per cent	B.P. degrees	%1,2	%1,3	Remarks
104	--	1.4852	1.4850	100	137	17	83	Air present
105	--	1.4845	1.4848	100	137	20	80	Air present
106	--	1.4839	1.4840	100	135	32	68	Air present
155	--	1.4852	1.4847	100	136	22	78	Air + H_2O
103	--	1.4832	1.4842	99	134	30	70	No air
185	+ +	1.4839	1.4848	98	136	21	79	No air
186	--	1.4672	1.4824	75	124	57	43	No air
111	--	1.4833	1.4829	100	128	49	51	H_2O
112	--	1.4822	1.4817	100	119	67	33	H_2O
182	+ + + +	1.4539	1.4861	50	138	0	100	Benzoyl
183	+ + + +	1.4804	1.4853	92	128	12	88	Peroxide
184	+ + + +	1.4855	1.4850	100	135	17	83	Present

*Standard conditions: Evacuation of gases in the system at liquid air temperature, no added salts, no added peroxides, no anti-oxidants, no solvents, no elevation of temperature above that of the room, and the bomb is kept away from light until the addition is complete. Variations from these standard conditions will be expressly noted where they occur.

**See page 10 for method of determining peroxide content.

ularities are directly traceable to the fact that the different samples of allyl chloride used, contained different amounts of peroxides. The difference in the final results in runs #185 and #186 are thus readily accounted for. The validity of this argument is brought out most strikingly by a consideration of Table III. In the presence of anti-oxidants (which have been shown to decompose peroxides in allyl chloride) and in vacuo 1-chloro-2-bromopropane becomes the predominant product. Even in the presence of air this product is formed to the extent of about 80 per cent. On the basis of these observations, we have decided to call the 1-chloro-2-bromopropane the "normal" product of the reaction and 1-chloro-3-bromopropane the "peroxide catalyzed" product.

TABLE III

STANDARD CONDITIONS*

Run	Anti-oxidant used	B.P. °C	n_D^{20} Crude	n_D^{20} Refined	Yield	%1,2	%1,3	Remarks
109	**	119	1.4820	1.4809	100	79	21	Air present
110	**	123	1.4814	1.4810	100	78	22	Air present
115	**	119	1.4800	1.4814	100	72	28	No air
116	**	118	1.4797	1.4800	100	93	7	No air
117	**	124	1.4787	1.4798	100	96	4	No air
118	***	136	1.5109	1.5122	---	--	--	No air
119	***	131	1.4954	1.4987	---	--	--	No air
179	****	117	1.4813	1.4800	100	92	8	No air
180	****	120	1.4810	1.4804	100	87	13	No air
181	****	117	1.4813	1.4801	100	91	9	No air

*See Standard Conditions under Table II.
**Diphenylamine (0.4 - 0.6 gm.).
***Quinol (approx. 1.0 gm.).
****p-thiocresol (0.4 gm.) + manganous chloride (0.04 gm.).

It is significant that the results obtained in vacuo[8] and air are not due to the effect of pressure within the reaction system for the same results as in vacuo were obtained when the tubes were filled with nitrogen or hydrogen (Table IV).

TABLE IV

STANDARD CONDITIONS*
DIPHENYLAMINE USED AS ANTI-OXIDANT

Run	B.P. °C	n_D^{20} Crude	n_D^{20} Refined	Yield per cent	%1,2	%1,3	Gas Added
126	118	1.4811	1.4804	100	86	14	Nitrogen
127	118	1.4818	1.4811	100	76	24	Nitrogen
128	118	1.4811	1.4806	100	83	17	Hydrogen
129	118	1.4812	1.4812	100	75	25	Hydrogen

*See Standard Conditions under Table II

[8] By "vacuo" we mean that the residual gases of the system were removed and the tubes sealed off while the system was kept at the temperature of liquid air. Naturally, as the tubes were allowed to warm up to room temperature, there was a great deal of pressure in the reaction tubes.

b. The effect of solvents.- The results of the addition of hydrogen bromide to allyl chloride in solvents (Table V) confirm the conclusion, previously reached, that the peroxide content of the allyl chloride as well as that of the added peroxides, in this case the peroxides of the solvent, are reponsible for the formation of 1,3 chlorobromopropane. Our interpretation of the results, where acetyl bromide and glacial acetic acid are employed, is that the solvents themselves may decompose the peroxides under the experimental conditions. The differences one observes, therefore, with different solvents lead to deceptive conclusions unless one is familiar with the peroxide effect. Thus, as soon as diphenylamine is added, as an extreme precaution, identical results are obtained in all solvents.

We note, however, that even the anti-oxidants can only overcome the effect of small amounts of peroxides. The different results with ligroin (#136 and #163) with samples of allyl chloride containing different amounts of peroxide, are particularly illuminating as regards the factors influencing the addition, and the consistency of results one may hope to attain.

The commonly accepted notion, therefore, of the effect of solvents upon the direction of addition of reagents to unsaturated compounds is true but not in the sense intended. The solvents exert their peculiar effect, either because of the peroxide content, or indirectly through their effect on the peroxides in the allyl chloride in the solvents.

c. The effect of temperature and light.- In view of the exhaustive experiments on the effect of temperature and light in the case of the addition of hydrogen bromide to allyl bromide,[9] it was not deemed necessary to study these factors as exhaustively

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[9]Kharasch and Mayo, op.cit.

TABLE V

STANDARD CONDITIONS
(SOLVENTS EMPLOYED)

Run	Perox. cont.*	n_D^{20} Crude	n_D^{20} Refined	Yield	B.P. °C	%1,2	%1,3	Solvent	Gas Added
(a) No anti-oxidants added									
133	-	1.4820	1.4819	---	123	75	25	95% Acetic	None
134	-	1.4830	1.4879	---	122	80	20	95% Acetic	None
135	+	1.4849	1.4848	100	138	21	79	Ligroin	None
162	+	1.4851	1.4852	100	139	13	87	Ligroin	None
137	-	1.4801	1.4808	99	117	81	19	Acetyl bromide	None
138	-	1.4800	1.4802	100	117	90	10	Acetyl bromide	None
145	+	1.4825	1.4844	98	128	**40	60	Gl.Acetic	Air
146	+	1.4868	1.4872	---	129	**50	50	Gl.Acetic	Air
147	-	1.4823	1.4849	98	135	**20	80	Gl.Acetic	Air
148	-	1.4816	1.4846	---	127	**55	45	Gl.Acetic	N_2
149	-	1.4882	1.4899	---	125	**65	35	Gl.Acetic	N2
157	-	1.4825	1.4864	---	120	**85	15	Gl.Acetic	None
158	-	1.4854	1.4888	---	120	**85	15	Gl.Acetic	None
159	-	1.4842	1.4861	---	121	**85	15	Gl.Acetic	None
164	+	1.4855	1.4850	100	138	17	83	CCl_4	None
166	+	1.4856	1.4851	100	139	15	85	CCl_4	None
(b) Anti-oxidants present (Diphenylamine used)									
130	-	1.4775	1.4828	84	120	**85	15	Gl.Acetic	None
131	-	1.4842	1.4860	---	119	**90	10	Gl.Acetic	None
132	-	1.4831	1.4833	---	119	**90	10	Gl.Acetic	None
136	-	1.4806	1.4804	100	118	87	13	Ligroin	None
163	-	1.4823	1.4821	100	120	61	39	Ligroin	None

*Analysis of the mixture by boiling point rather than by the indes of refraction since the last traces of acetic acid were almost impossible to wash out by water. The acetic acid was detected in the last distillation when the boiling point was determined. The final result was not affected.

**See page 10 for method of determining peroxide content.

in the case of allyl chloride. We believe we have established, however, that the temperature and light exert their effects indirectly through their effects on the peroxides in allyl chloride. Both high temperature and exposure to light exaggerate the peroxide effect, and in view of the greater sensitivity of allyl chloride than allyl bromide to the effect of peroxides, the effects are much more exaggerated. The trend, however, is unmistakable, and with better anti-oxidants than the ones which were employed, higher yields of the 1-chloro-2-bromopropane would probably have been obtained at 100° (#143) and under strong illumination (#121).

The effect of light and temperature upon the addition of hydrogen bromide to allyl chloride is definitely an accelerating effect. The peroxide catalyzed reaction is affected by heat and light much more than the normal addition. Hence, the application of heat or light to the addition reaction results in the formation of only the peroxide catalyzed product, i.e., 1,3-chlorobromopropane.

d. The effect of salts.- It is known that certain metallic salts catalyze the addition of hydrogen bromide to olefines. In the case of allyl chloride, unfortunately, the results are complicated by a polymerization of allyl chloride, induced by the metallic salt. In the presence of an anti-oxidant considerable quantities of the normal addition product were obtained.

Summary

From the foregoing discussion, it is evident that the direction in which hydrogen bromide is absorbed by the double bond in allyl chloride depends primarily on the presence or absence of peroxides or, in the presence of oxygen, of peroxide-forming components in the reaction mixture. In the absence of peroxides or in the presence of anti-oxidants to overcome their action, 1-chloro-

2-bromopropane is formed as the chief or normal product of the reaction. In the presence of peroxides 1-chloro-3-bromopropane is the predominant addition product.

The normal addition to give 1-chloro-2-bromopropane takes place very slowly (up to a month), while the peroxide catalyzed reaction is comparatively fast and results in the formation of the 1,3 isomer.

Where the amounts of peroxides are positively controlled by the use of anti-oxidants or materials which decompose peroxides, we obtain as the chief product the normal 1,2 isomer.

These results are in complete agreement with the predictions of the Kharasch theory of partial polarity, while the Lewis and Lucas view, which predicted only one product, is inadequate.

TABLE VI

THE EFFECT OF TEMPERATURE AND LIGHT

Run	React. time	n_D^{20} Crude	n_D^{20} Refined	Yield per cent	B.P. °C	%1,2	%1,3	Temp. °C	Anti-oxidants
(a) Temperature (Standard Conditions. Where used, diphenylamine is the anti-oxidant.)									
139	50 hrs.	1.4760	1.4860	85	138	1	99	-76	None
140	50 hrs.	1.4709	1.4849	85	138	19	81	-76	None
141	60 days	1.4258	------	15	120	*85	15	-5	None
142	60 days	1.4253	------	15	122	*80	20	-5	None
143	40 hrs.	1.4838	1.4840	100	119	33	67	-100	Yes
144	40 hrs.	1.4820	1.4846	98	122	24	76	-100	Yes
(b) Effect of Light (Standard Conditions. Where used (Compare Tales I) diphenylamine is the anti-oxidant.)									
107	13 hrs.	1.4860	1.4861	100	138	0	100	None	None
120	12 hrs.	1.4800	1.4832	98	135	45	55	None	Yes
121	12 hrs.	1.4797	1.4831	95	136	46	54	None	Yes
150	14 hrs.	1.4737	1.4796	96	124	**72	28	Gl.acetic	None
151	24 hrs.	1.4769	1.4829	95	124	**72	28	Gl.acetic	None
152	24 hrs.	1.4581	1.4816	63	139	**30	70	Ligroin	None
153	24 hrs.	1.4750	1.4839	87	140	32	68	Ligroin	None
160	24 hrs.	1.4830	1.4850	98	139	15	85	Acet.br.	None
161	24 hrs.	1.4802	1.4850	92	139	15	85	Acet.br.	None

*Due to the low yield, the usual refining methods could not be employed here. Therefore, the analysis was made by the boiling point of the material at the first distillation.

**Analysis by boiling point.

EXPERIMENTAL PART

In order to evaluate singly the effect of light, temperature, solvent, metallic salts, anti-oxidants, peroxides, moisture, and the residual gas in the reaction vessel upon the addition of hydrogen bromide to allyl chloride, a special technique had to be developed and reagents of a high degree of purity prepared.

1. Preparation of Reagents

The reagents were prepared to assure their dryness. Hydrogen bromide was prepared by the reaction of bromine and tetrahydronaphthalene, held at 120-130°. The vapors ascended through a 50 cm. air-cooled dephlegmating column and passed through a tube which contained successive layers of red phosphorus on glass beads and phosphoric anhydride spread on asbestos.

The allyl chloride was prepared by the method of Dewael.[10] Allyl alcohol (Eastman technical grade) was treated with dry hydrogen chloride in the presence of one per cent of cuprous chloride. The dry hydrogen chloride was absorbed quantitatively; considerable heat was evolved. Under vigorous cooling the reaction was allowed to proceed until an excess of hydrogen chloride had been added and allyl chloride separated. The allyl chloride was washed first with water, then with a saturated solution of sodium bicarbonate, then again with water to remove any alkalis, and finally dried over anhydrous sodium sulfate. It was distilled through a five foot column, fitted with a water-cooled dephlegmating head. A fraction boiling at 145-145.2° was obtained. The yield was about 75 per cent of the calculated amount. N_D^{20} of the allyl chloride thus prepared was 1.4154.

All the materials used in this work were tested for peroxides. The materials were shaken with ferrous ammonium sulfate and

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[10]Dewael, Bull. Soc. Chim. Belg. 39, 40 (1930).

10 per cent ammonium thiocyanate solution. A perceptible difference in shade between the test solution and a blank was considered a positive peroxide test. A marked darkening of the test solution was considered 2+; a very dark reddening of the test solution was considered 3+; an opaque red color in the test solution was considered 4+ (indicative of a large peroxide content). No difference in shade between the test solution and the blank was considered a negative peroxide test.

1. Preparation of Reference Compounds

In order to obtain the physical data necessary for a determination of the progress of the addition reaction, we had to prepare 1,2-chlorobromopropane and 1,3-chlorobromopropane in pure form. The method employed consisted of treating the appropriate chlorohydrin with hydrogen bromide and isolating the chlorobromopropane. In this connection, we must consider the work of Smith.[11] Smith showed, by measurements of the hydrolysis rate, that it is almost impossible to separate mixtures of the halohydrins. It is likely, therefore, that in what we consider to be pure reference compounds there may be as much as 5 per cent of the other isomer. The only physical property this would affect is the refractive index. Since our results are only semi-quantitative, we feel that the conclusions we draw from our work are in no way invalidated.

Trimethylene chlorohydrin, $ClCH_2CH_2CH_2OH$, prepared by the method of Organic Syntheses,[12] was treated with 1.25 moles of dry hydrogen bromide in the presence of 1 per cent of cuprous chloride in an open flask. The product was heated to 70°, washed with water, dried over calcium chloride, and distilled. A constant

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[11] L. Smith, Z. phys. Chem. 92, 719 (1917).

[12] Organic Syntheses, New York: Wiley, 1927. VIII, p.112.

boiling fraction at 141° with an index of frfraction of 1.4861 was obtained. The yield was approximately 60 per cent of the calculated amount. This corresponds to the 1,3-chlorobromopropane previously recorded in the literature.

Two distinct syntheses of 1,2-chlorobromopropane were made. In the first case propylene oxide was treated with hydrogen chloride according to the method of Clapp.[13] The resulting chlorohydrin was treated with dry hydrogen bromide. The product was distilled; the resulting dihalogenated propane boiled between 117° and 120° at 742 mm. A yield of 70 per cent of the calculated amount was noted. The product showed an index of refraction of 1.4811 at 20°. A second method of synthesis involved the use of propylene chlorohydrin (Eastman). The Eastman propylene chlorohydrin was fractionated and showed a constant index of refraction at 20° of 1.4395 contrasted with an index of refraction at 20° of 1.4411 for the propylene chlorohydrin, prepared by the method of Clapp, and an index of refraction at 20° of 1.4392 for propylene chlorohydrin, as determined by Henry.[14] Therefore, we used the Eastman propylene chlorohydrin in the following reaction.

Propylene chlorohydrin (Eastman) was treated with 0.25 mole anhydrous zinc bromide and 1.25 moles of hydrogen bromide. The bombs (containing 40 grams of chlorohydrin) were sealed off and heated to 60°-75° for 48 hours. The contents of the bombs took on a dark red color. The bombs were opened and the contents thoroughly washed with water (8-10 volumes) until the water was neutral to litmus (an excess of hydrogen bromide was observed when the bombs were opened). The resulting light brown oil was dried over anhydrous sodium sulfate anddistilled in vacuo. The distillate (caught in a carbon dioxide snow-acetone trap) was then distilled

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[13]Clapp, Ph.D. dissertation, University of Chicago, 1929.
[14]Henry, Rec. trav. chim. 22, 325 (1903).

at room pressure. A fraction boiling between 115° and 117° at 746 mm. and with a constant index of refraction at 20° throughout this range was reserved for analysis.

The method of analysis was combustion in a Parr bomb by sodium peroxide with titration of the resulting solution for total halogen content.

Analysis:	I	II	
Theory . . .	0.006086	0.006200	Moles
Found . . .	0.006000	0.006133	Total halogen

3. The Analysis of the Reaction Products

In the study of the addition of hydrogen bromide to allyl chloride the yield of the reaction as well as the relative proportion of the two isomers were determined from the index of refraction. In a few cases, the composition of the reaction product had to be determined by the boiling point since solvents which could not be washed out disturbed the index of refraction. The yield could easily be determined by comparing the index of refraction of the reaction products, after removal of hydrogen bromide, with the index of refraction of the mixture of addition products after the removal of allyl chloride. The index of refraction of a mixture of the two addition products, whose resultant index is known, and allyl chloride is practically a linear function of the molal composition. After removal of allyl chloride, the index of refraction of the solution of 1,2 and 1,3-chlorobromopropanes gives the molal composition. The index of refraction of the chlorobromopropanes plotted against the molal composition is also a linear function.

Standard Procedure for the Addition Reaction

The allyl chloride, prepared above, was transferred to a pyrex tube A approximately 40 cm. long. By means of a glass tube reaching to the bottom of A, hydrogen bromide was passed into the allyl chloride from the hydrogen bromide generator until the desired weight of hydrogen bromide had been added. The operation was carried out at -80°. Phosphorus pentoxide was added to the mixture and a wad of glass wool was pushed down into the tube. The tube was put into a Dewar bottle, containing liquid nitrogen, and the contents of the tube were frozen. The tube was then sealed to a transfer apparatus.

The transfer apparatus was essentially a large inverted U-tube with a side tube at the top. At the bottom of one arm of the U was sealed the pyrex tube A. At the bottom of the other arm of the U was sealed a short length of pyrex capillary tubing to which was sealed a pyrex bomb tube. The bomb tube was made of extra heavy pyrex tubing designed for combustion work. The bombs were generally 20-40 centimeters long. The capillary seals were made for a reason which will soon be apparent.

With all the seals to the U-tube made, the entire apparatus with the first tube still in liquid nitrogen was sealed to a vacuum line and pumped down, by means of a three stage mercury pump, backed by a mechanical oil pump, to 10^{-5} atmospheres, as measured by a McLeod gauge. When the desired vacuum had been attained, the entire transfer apparatus was flamed out, except that part in the liquid nitrogen Dewar, and the transfer apparatus was sealed off from the vacuum line. The bomb tube was chilled with a carbon dioxide snow-acetone bath and then placed in a liquid nitrogen bath. The other liquid nitrogen bath was then removed and the contents of the first tube were allowed to distill into the bomb tube. The

glass wool wad slows down the distillation and ensures efficient contact of the reagents with the phosphorus pentoxide.

When the distillation was complete, the bomb tube was sealed off from the transfer apparatus at the capillary. The capillary eliminated the possibility of a collapse of the walls of the tube under the high vacuum employed. The bomb was put away in the dark or in the light until it was ready to be opened. Bombs were opened by scratching the surface with a file and applying a hot spot of glass to the scratch.

It can readily be seen that solvents can be distilled into the bomb tube with the reagents; any other materials can be put into the bomb tube before it is sealed to the transfer apparatus. Gases may be added to the system through a long side tube, containing phosphorus pentoxide, attached to the tube through which the system is pumped out. This long tube was drawn out to a capillary tip and could be attached to any gas source for gases to be added to the system. When the capillary is broken after the distillation is complete, the gas is drawn through the phosphorus pentoxide tube into the system, after which the bomb tube is sealed off as before. This is the standard method of preparation and results in a careful control of the factors which we enumerated above.

5. Removal of Allyl Chloride from a Mixture of Dihalogenated Propanes

After the preparation, purification, analysis, and determination of the physical constants of the pure addition products, it was necessary to devise a method for the removal of allyl chloride from a mixture of the two addition products. Distillation methods for the removal of allyl chloride were thought not to be effective since small traces of allyl chloride would affect the index of refraction very markedly. For the quantitative removal of allyl chloride many substances were tried, among them being the

following: pyridine, trimethylamine, triethanolamine, dimethyl aniline, quinoline, piperidine, alpha and beta naphthylamines, concentrated sulphuric acid plus 10 per cent sulphur trioxide plus 1 per cent copper sulphate.

Only the last method was successful. To conserve our reference compounds we tested the method upon mixtures of propylene chloride and trimethylene bromide with allyl chloride. The results of five such experiments were as follows when approximately twenty five per cent of allyl chloride was added to a synthetic mixture of the stated original index of refraction:

No.	n_D^{20} original	n_D^{20} after standard washing
1	1.4389	1.4384
2	1.5216	1.5213
3	1.4575	1.4579
4	1.4412	1.4410
5	1.5178	1.5178

The standard procedure in every case above and for every run to be later described was as follows:

(a) The material was washed with water and dried over calcium chloride.

(b) The material was distilled completely in a micro-distilling flask.

(c) The index of refraction was taken for a later determination of the percentage of allyl chloride present.

(d) The addition compounds were shaken with three to five times their volume of concentrated sulfuric acid containing 10 per cent of sulfur trioxide and 1 per cent of copper sulphate. The shaking was done at -5° to -10° for just ten minutes.

(e) The resulting mixture was poured upon ice, shaken, and the water layer discarded.

(f) The addition products were then washed with water.

(g) The addition products were then washed with a saturated

solution of sodium bicarbonate.

(h) The addition products were again washed with water, and dried over calcium chloride.

(i) The addition products were again distilled and the index of refraction taken.

THE ADDITION OF HYDROGEN BROMIDE TO ISOBUTYLENE

Kharasch and Shane[15] found that the presence of peroxides largely affected the addition of hydrogen bromide to balanced molecules like allyl chloride, allyl bromide, and propylene. Furthermore, Kharasch, McNab, and Mayo[16] have shown that the addition of hydrogen bromide to propylene gives quantitative yields of the normal propyl bromide if the addition is carried out in the presence of large quantities of peroxides.

It is because of this latter observation that we decided to investigate more fully the addition of hydrogen bromide to isobutylene. It is pertinent to point out here that this latter molecule is very unbalanced electronically, according to the postulates of Kharasch and Reinmuth.[17]

$$H_3C-C(CH_3)=CH_2 \quad + \quad HBr \longrightarrow H_3C-\underset{Br}{C}(CH_3)-CH_3$$

This theory would predict, therefore, that external conditions should have little effect upon the direction of addition. Tertiary butyl bromide should be the sole product of the reaction.

As in the case of allyl chloride,[18] a large number of factors were kept under control in this investigation and the effects of those factors evaluated.

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[15] Kharasch and Shane, preceding paper.
Kharasch and Mayo, unpublished work.
Kharasch, McNab, and Mayo, unpublished work.

[16] Kharasch, McNab, and Mayo, loc. cit.

[17] Kharasch and Reinmuth, J. Chem. E., 5, 404 (1928).
Kharasch and Reinmuth, ibid., 8, 1703 (1931).
Kharasch and Darkis, Chem. Rev. 5, 571 (1928).

[18] Kharasch and Shane, loc. cit.

PREVIOUS WORK

Previous work[19] upon the addition of hydrogen halide to isobutylene showed complete agreement in that the only product of the reaction was tertiary butyl halide. Ipatieff and Ogonowsky,[20] however, claim that the direction of addition is influenced by glacial acetic acid. They claim that two separate additions of hydrogen bromide to isobutylene in glacial acetic acid showed respectively the presence of 5 per cent and 15 per cent of isobutyl bromide.

In all the work thus far reported, with the exception of that of Maas and his collaborators,[21] the conditions of temperature, moisture, solvents, catalytic agents, gases over the reaction mixture, and light were not controlled. Maas added hydrogen chloride to isobutylene in a vacuum apparatus. Tertiary butyl chloride is the only product of the reaction.

Analysis of Addition Products

The method of analysis to determine the relative amounts of tertiary butyl bromide and isobutyl bromide involved taking the refractive index of a mixture of the two substances. To insure the validity of this determination the original reagents had to be removed. This was accomplished by a vacuum distillation in a stream of carbon dioxide at room temperature and 30 mm. pressure.

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[19] Butlerow, Ann. 164, 1ff (1867).
Roozeboom, Ber., 14, 2396 (1881).
Chechoukoff, Bull. soc. chim. (2), 46, 823 (1886).
Ipatieff and Ogonowsky, Ber., 36, 1988 (1903).
Michael and Zeidler, Ann., 393, 109 (1912).
LeBel, Bull. soc. chim. (2), 28, 462 (1877).
Puchot, Ann. chim. phys, (5), 28, 508, 549 (1883).
Michael and Brunel, Am. Chem. J. 48, 267 (1912).
Brunel, J. Amer. Chem. Soc., 39, 1990 (1917).
Coffin, Sutherland, and Maas, Canadian J. Res. 2, 267 (1930).

[20] Ipatieff and Ogonowsky, loc. cit.

[21] Maas et al., loc. cit.

The index of refraction plotted against the molal composition of synthetic mixtures of isobutyl bromide and tertiary butyl bromide yields a straight line. N_D^{20} of tertiary butyl bromide is 1.4280. N_D^{20} of isobutyl bromide is 1.4360.

Standard Conditions of Addition of Hydrogen Bromide to Isobutylene

To conserve space, the standard conditions of the addition are, unless a deviation from these conditions is explicitly noted, as follows: the reaction is run in vacuo, in the dark in the absence of solvents, in the absence of either peroxides or anti-oxidants, in the absence of metallic salts, and in the absence of moisture.

Influence of Time

Keeping in mind here, as always, that only runs with yields greater than 85 per cent of the theoretical have any significance in our work, because of a possibility that two addition reactions with unequal reaction rates might exist, we studied the product of the reaction at various time intervals. In the belief that isobutyl bromide might be found in the early stages of the reaction, if not in the later, the addition was stopped three hours, twenty four hours, thirty six hours, and three days, after the bomb tube was sealed off. In each case only tertiary butyl bromide was found.

Influence of Light

Where the bomb tube was exposed to a 500 watt tungsten filament lamp at a distance of 10 cm., under otherwise standard conditions, the product was only tertiary butyl bromide. (See also a succeeding page for the addition of hydrogen bromide to isobutylene in the presence of light and glacial acetic acid.)

Influence of Solvents

In an attempt to slow down the addition of hydrogen bromide

to isobutylene, glacial acetic acid was used as a solvent for the reaction. The product was always completely soluble in water;[22] the product was tertiary butyl bromide according to the index of refraction. However, since the error of the method of analysis by refractive index is about 5 per cent, we feel that the statement of Ipatieff and Ogonowsky[23] to the effect that small yields of isobutyl bromide were obtained as a product of the addition is not gainsaid by our work. It seems difficult, however, to see how these investigators separated by hydrolyses and by distillation without precision stills, thirteen grams of isobutyl bromide in 210 grams of total product. The possibility of any unhydrolyzable octyl bromide was not investigated by Ipatieff and Ogonowsky, although Maas[24] showed that such a compound may be a by-product of the reaction, under certain conditions.

When m-xylene (boiling point 137°-138°) was used as a solvent the only product was tertiary butyl bromide. The m-xylene was removed from the addition product by fractionation through a 10 inch, puckered-wall, pyrex distilling column.

In an attempt to speed up the reaction in glacial acetic acid, a bomb tube, containing isobutylene, hydrogen bromide, and glacial acetic acid, was exposed to a 500 watt tungsten filament lamp for 48 hours. The product was totally soluble in water and showed an index of refraction at 20° of 1.4283. Hence, we again obtained tertiary butyl bromide.

Influence of Air and Oxygen

We felt that air might have an effect upon the reaction.

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[22] Cf. Ipatieff, loc. cit.
Brunel, loc. cit.
Maas, loc. cit.

[23] Ipatieff and Ogonowsky, Ber., 36, 1988 (1903).

[24] Maas, et al., Canadian J. Res., 2, 267 (1930).

Runs were made in which dry air and dry oxygen were present in the bomb tube. In every case only tertiary butyl bromide was found.

Influence of Gases Other Than Oxygen

To determine the effect of pressure upon the reaction, runs were made in the presence of pure, dry nitrogen which had been washed with alkaline pyrogallol. No product other than tertiary butyl bromide was found.

Influence of Temperature

Runs were made in which the bomb tube was kept in the vapors of a boiling carbon tetrachloride bath. Other runs were made in which the bomb tubes were kept in an ice-salt mixture at -10°. Under both conditions, the reaction was complete in less than 48 hours. The reaction product was, as always, tertiary butyl bromide.

Influence of Metallic Salts

To study the effect of metallic salts upon the addition of hydrogen bromide to isobutylene, runs were made in which 0.1 gram of ferric chloride was put in bomb tubes. These runs showed a large evolution of heat at carbon dioxide-snow temperatures, indicating a very fast reaction. Analysis showed the product to be pure tertiary butyl bromide.

Influence of Moisture

The presence of two drops of water in bomb tubes, run under otherwise standard conditions, did not affect the product.

Influence of Peroxides and Anti-oxidants

In the belief that tertiary butyl bromide might be the product of a peroxide-catalyzed reaction, we tried to minimize that reaction by the use of anti-oxidants which had been shown to be effective in the addition of hydrogen bromide to allyl chloride.[25] Diphenylamine had no effect. P-thio cresol in the presence of a

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[25] Kharasch and Shane, loc. cit.

trace of manganous chloride showed no effect under standard conditions with and without the use of a solvent, m-xylene.

It was reasoned that if anti-oxidants had no effect, perhaps peroxides would have an effect. Benzoyl peroxide was used with and without m-xylene. The only product isolated was tertiary butyl bromide. Next we tried ascaridole, a powerful, naturally occurring peroxide. Again, the only product isolated was tertiary butyl bromide.

Summary

It can be seen that, under a wide variety of conditions, the addition of hydrogen bromide to isobutylene results only in tertiary butyl bromide. It should be remembered, however, that the error of the method of analysis is about 5 per cent. So far as we can tell now, there is no method for producing isobutyl bromide by this reaction at temperatures below 76°.[26]

It must be concluded that the methods now at our disposal for the shift of the electrons of the double bond are inadequate in the case of a highly unbalanced molecule like isobutylene. It would seem that there are limits which we cannot transcend in our direction of the addition of hydrogen bromide to unsymmetrical olefines. The only additions which we can influence with a fair amount of certainty are those in which the electrons of the double bond are between carbon atoms carrying radicals of approximately equal electronegativities. However, this is only what we would expect from a consideration of the Kharasch theory of partial polarity.

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[26] Cf. Brunel, loc. cit., on the reaction as run at much higher temperatures.

EXPERIMENTAL PART

The experimental work consisted of forty separate additions of hydrogen bromide to isobutylene. The technique of addition was identical with that employed for the addition of hydrogen bromide to allyl chloride.[26]

Preparation of Reagents

Isobutylene was prepared from tertiary butyl chloride and alcoholic potassium hydroxide. Tertiary butyl chloride was prepared from tertiary butyl alcohol and concentrated hydrochloric acid by distilling through a column the oily layer off the mixture of reagents. The crude tertiary butyl chloride was dried over anhydrous sodium sulfate and distilled, a fraction being taken which showed a constant boiling point and a constant index of refraction.

Tertiary butyl chloride was added to a rapidly refluxing saturated solution of potassium hydroxide in 95 per cent alcohol. The vapors passed directly to a spiral condenser, connected by a ground glass joint to the reaction vessel. From the spiral condenser the vapors were led to a gas scrubbing tower where the alcohol was washed out by water. From the tower the vapors passed through a trap kept at -5° to another trap where the isobutylene was condensed in a trap kept at the temperature of an acetone-carbon dioxide snow freezing mixture. No rubber or cork was used at any place along the line.

The hydrogen bromide was prepared as for the reaction with allyl chloride. The various solvents were carefully dried and redistilled to insure their purity.

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[26] Kharasch and Shane, loc. cit.